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Static gas-liquid interfacial direct current discharge plasmas using ionic liquid cathode

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Due to the unique properties of ionic liquids such as their extremely low vapor pressure and high heat capacity, we have succeeded in creating the static and stable gas (plasmas)-liquid (ionic liquids) interfacial field using a direct current discharge under a low gas pressure condition. It is clarified that the ionic liquid works as a nonmetal liquid electrode, and furthermore, a secondary electron emission coefficient of the ionic liquid is larger than that of conventional metal electrodes. The plasma potential structure of the gas-liquid interfacial region, and resultant interactions between the plasma and the ionic liquid are revealed by changing a polarity of the electrode in the ionic liquid. By utilizing the ionic liquid as a cathode electrode, the positive ions in the plasma region are found to be irradiated to the ionic liquid. This ion irradiation causes physical and chemical reactions at the gas-liquid interfacial region without the vaporization of the ionic liquid. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3133213]

I. INTRODUCTION

Discharge plasmas in contact with or inside liquids are recognized to have a potential for applications to wastewater treatment, sterilization, microanalysis of liquid ingredient, and nanomaterial creation based on their distinctive properties such as ultrahigh density, high reactivity, high process rate, and so on. The liquid phase plasma researches have been started by Gubkin[1] in 1887. In the middle of the 20th century, Denaro and Hickling,[2] Kanzaki *et al.*,[3] and Cserfalvi and Mezei[4] performed systematic fundamental researches on the liquid phase plasmas, and Sato *et al.*[5] and Locke *et al.*[6] investigated the various kinds of liquid phase plasmas for several environmental applications. Furthermore, recent advances in the generation of plasmas using arc,[7] streamer,[8,9] pulsed direct current (dc) grow,[10] and microwave[11,12] discharges in the liquids such as water, organic solvent,[13] and supercritical carbon dioxide[14] have pioneered new fields as mentioned above. In these cases, the discharge is sustained in gas bubbles generated in the liquid, and therefore it has been recognized that an understanding of the interfacial surface of the bubbles as a plasma generation space in the liquid is significant for making best use of the liquid phase plasmas as a reaction field. However, it is difficult to analyze the properties in the interfacial region of the bubbles because of their dynamical behaviors in the liquid, and as a result, the precise structure of the interface between the liquid and the bubbles (gas or plasma) remains an open question. In this sense, we have claimed that the generation of static and stable gas-liquid interface is necessary to clarify the phenomena at the gas-liquid interface as the fundamental research on the liquid phase plasmas. Although we have already reported the gas-liquid interfacial plasmas using an alternating current (ac) discharge,[15–17] we were unable to clarify the detailed properties, such as potential profiles because of the unexpected fluctuation and anomalous discharge in the liquid due to the ac electric field.

In this paper, we present the development of a new plasma system to form the spatially and temporally stable plasma-liquid interfacial surface, i.e., a dc discharge plasma is generated just above the liquid by applying the dc power to an electrode immersed in the liquid against a grounded electrode set in the gas phase region. The precise potential structure between these electrodes through the plasma-liquid interfacial region is clarified for the first time, and the dynamics of the plasma ions is found to be controlled using the cathode sheath electric field in the interfacial region. The control of the plasma ion irradiation to the liquid and the consequent physical and chemical reactions are useful for the application such as the creation of various kinds of nanoparticles.[10,18–20]

II. EXPERIMENTAL APPARATUS

For the purpose of the generation of the static and stable plasma contacting with the liquid, we adopt ionic liquids[21,22] which have recently gotten much attention in the electrochemistry field. The ionic liquids have the interesting characteristics such as their composition consisting of only positive and negative ions, i.e., no neutral solvent, extremely low vapor pressure, high heat capacity, and nonflammability. These characteristics enable us to introduce the ionic liquids to the vacuum system and the discharge plasma. Therefore, the ionic liquids are the most suitable liquid for the formation of nanocomposite materials using the discharge plasmas in contact with the liquids.

Figure 1 shows schematic diagrams of experimental setup which has a glass cell of 20 mm in diameter and 10 mm in depth in a cylindrical glass chamber of 15 cm in diameter and 50 cm in length. A cathode electrode which is made of a platinum (Pt) plate with 15 mm diameter is located

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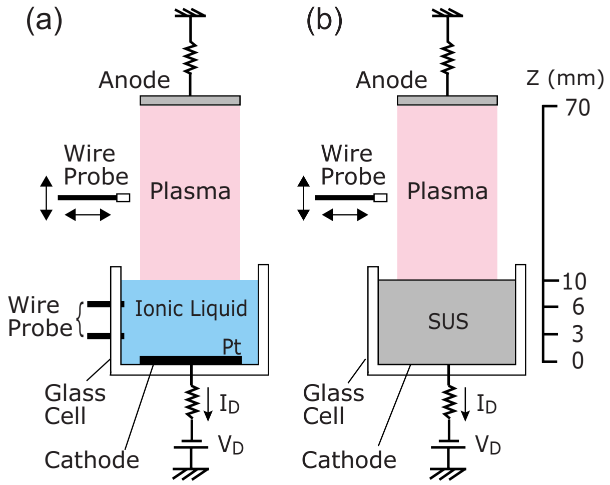

FIG. 1. (Color online) Schematic diagrams of experimental setup for dc discharge plasmas, where the cathode is set in the glass cell, and is (a) the Pt plate in the ionic liquid and (b) the SUS plate directly contacting the plasma. The anode is located at the top of the gas plasma region. These configurations are defined as A-mode.

inside the glass cell and a popular ionic liquid (1-buthl-3-methyl-imidazolium tetrafluoroborate: $[C_8H_{15}N_2]^+[BF_4]^-$) which is in a liquid state at room temperature, has an alkyl chain, and is relatively cheap, is introduced on the cathode electrode as shown in Fig. 1(a). The amount of the ionic liquid is 3 ml. Removal of the water dissolved in the ionic liquid is performed under the vacuum condition for 2 h after introducing the ionic liquid into the glass chamber. A dc power is supplied to the cathode electrode in the ionic liquid. On the other hand, a grounded anode electrode which is made of a stainless steel (SUS) plate is set in a gas phase (plasma) region at a distance of 70 mm from the cathode electrode.

For the purpose of investigating the effects of the ionic liquid on the discharge, the ionic liquid on the Pt plate is replaced by the SUS plate as shown in Fig. 1(b). Here, the surface position of the SUS plate is adjusted to that of the ionic liquid. These discharge configurations, in which the cathode electrode (the Pt plate with the ionic liquid or the SUS plate) is in the glass cell, are defined as "A-mode." Argon gas is adopted as a discharge medium, and the gas pressure P_{gas} is varied from 20 Pa to 80 Pa approximately.

A high voltage probe is directly connected to the cathode electrode to measure the bias voltage of it. A Langmuir probe is inserted at the position of $z=20-60$ mm to measure parameters of the plasma in contact with the ionic liquid ($z=0$: surface of electrode in the ionic liquid). The floating potential in the ionic liquid can also be measured using electrostatic probes ($z=3$ and 6 mm), where only the tip of the probe is inserted into the glass cell to minimize the disturbance of the probe.

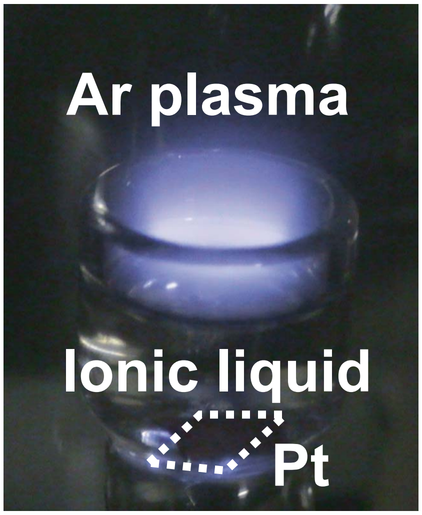

FIG. 2. (Color online) Photo of the stable dc discharge plasma on the ionic liquid in the A-mode. $P_{\text{gas}}=40$ Pa, $I_D=1$ mA.

III. EXPERIMENTAL RESULTS

We have achieved the generation of liquid incorporated dc discharge plasmas at low gas pressures with a high stability using the ionic liquid, similar to the normal glow discharge plasmas in the absence of the liquid. Figure 2 shows a photo of the dc discharge plasma on the ionic liquid in the A-mode [see Fig. 1(a)] for $P_{\text{gas}}=40$ Pa, discharge voltage $V_D=-260$ V, and discharge current $I_D=1$ mA. It is found that the static interfacial region between the plasma and the ionic liquid is stably generated.

Figure 3 presents axial profiles of the space potential ϕ in the plasma region and the floating potential in the ionic liquid in the A-mode for $P_{\text{gas}}=40$ Pa and $I_D=1$ mA, where the cathode is (a) the Pt plate in the ionic liquid and (b) the SUS plate directly contacting the plasma. In the case that the cathode is the SUS plate, the discharge voltage, namely, the potential of the cathode electrode is $V_D=-515$ V. In the presence of the ionic liquid on the Pt plate, on the other hand, V_D drastically reduces to about -290 V and the potential in the ionic liquid is -288 V which is almost the same as that of the cathode electrode in the ionic liquid. This result means that a cathode fall is formed just above the ionic liquid instead of the Pt plate, namely, the ionic liquid introduced on the Pt plate in the glass cell is found to work as the liquid cathode electrode.

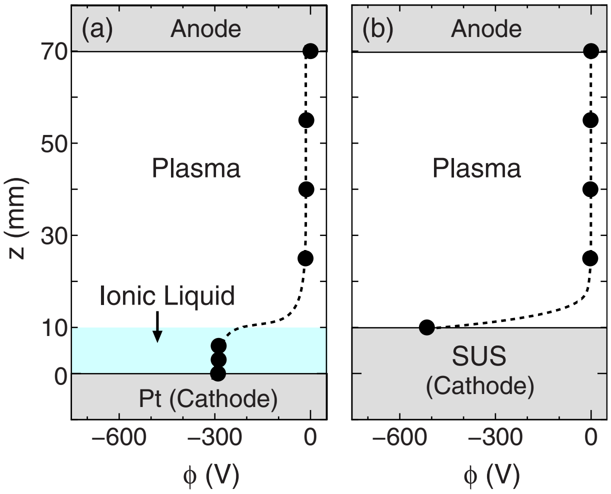

FIG. 3. (Color online) Axial profiles of the space potential ϕ in the plasma region and the floating potential in the ionic liquid in the A-mode for $P_{\text{gas}}=40$ Pa and $I_D=1$ mA, where the cathode is (a) Pt plate in the ionic liquid and (b) SUS plate directly contacting the plasma.

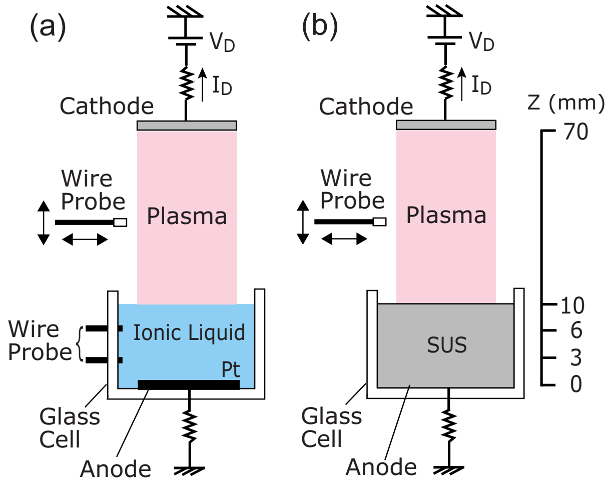

FIG. 4. (Color online) Schematic diagrams of experimental setup for dc discharge plasmas, where the cathode is located at the top of the gas plasma region. The anode is set in the glass cell, and is (a) the Pt plate in the ionic liquid and (b) the SUS plate directly contacting the plasma. These configurations are defined as B-mode.

Since the potential in the plasma region is about −5 V, the cathode fall voltage, i.e., the potential difference between the plasma and the ionic liquid in the cathode sheath region is about 285 V and the sheath electric field formed on the ionic liquid gives rise to the electrostatic acceleration of positive ions in the plasma, namely, an ion irradiation to the ionic liquid.

In order to examine the effects of the ion irradiation to the ionic liquid on discharge-related phenomena, the cathode electrode is switched to the SUS plate located at the top of the gas plasma region and the Pt plate in the ionic liquid is grounded instead, which is defined as "B-mode" as shown in Fig. 4(a). For the purpose of comparison, the configuration that the SUS plate in the glass cell is grounded, i.e., works as the anode electrode, is also introduced [Fig. 4(b)].

Figure 5 shows axial profiles of the space potential ϕ in the plasma region and the floating potential in the ionic liquid in the B-mode for $P_{\text{gas}}=40$ Pa and $I_D=1$ mA, where the anode is (a) the Pt plate in the ionic liquid and (b) the SUS plate directly contacting the plasma. The discharge voltage in the B-mode is about −700 V which is much larger than that in the presence of the ionic liquid in the A-mode. Furthermore, this discharge voltage is almost the same between with and without the ionic liquid on the anode in the glass cell. This is because the discharge voltage in the B-mode is determined by the properties of the cathode electrode located at the top of the gas plasma region.

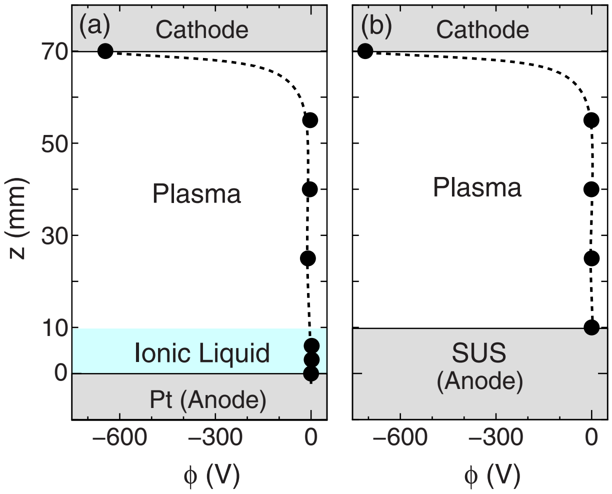

FIG. 5. (Color online) Axial profiles of the space potential ϕ in the plasma region and the floating potential in the ionic liquid in the B-mode for $P_{\text{gas}}=40$ Pa and $I_D=1$ mA, where the anode is (a) Pt plate in the ionic liquid and (b) SUS plate directly contacting the plasma.

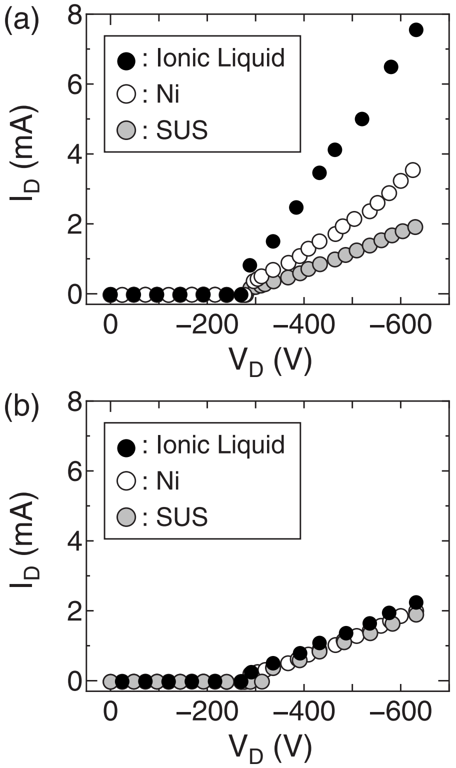

FIG. 6. Dependence of the discharge voltage V_D current I_D characteristics on the materials of (a) the cathode electrode in the A-mode and (b) the anode electrode in the B-mode. $P_{\text{gas}}=40$ Pa.

When the ionic liquid exists on the Pt plate [Fig. 5(a)], the potential in the ionic liquid is found to be 0 V because the Pt plate is grounded. Since the potential in the plasma region is about −5 V which is the same as that in the A-mode, the potential difference between the plasma and the ionic liquid is very small (~5 V) and the sheath electric field direction is opposite to that in the A-mode. Therefore, electrons in the plasma are showered to the ionic liquid instead of the positive ion irradiation.

These ion irradiation and electron shower to the ionic liquid in the A- and B-modes, respectively, are expected to affect the discharge in the gas phase region. Therefore, the discharge voltage V_D current I_D characteristics are measured in both the A- and B-modes, which are presented in Fig. 6, where we change materials of the electrodes in the glass cell, i.e., (a) the cathode electrode in the A-mode and (b) the anode electrode in the B-mode. When the materials of the cathode electrodes in the A-mode are changed to SUS, nickel (Ni), and the ionic liquid [Fig. 6(a)], the discharge current in the case of the ionic liquid is found to be the largest in

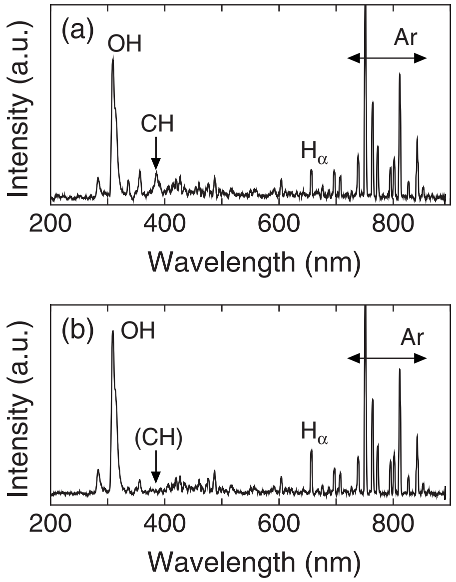

FIG. 7. OES spectra in the gas plasma region in (a) the A-mode and (b) the B-mode, where the ionic liquid is introduced in the glass cell. $P_{gas}=20$ Pa, $I_D=1.5$ mA.

comparison with those in the cases of Ni and SUS. On the other hand, the change in materials of the anode electrodes in the B-mode has no effect on the discharge characteristics as shown in Fig. 6(b).

These results suggest that the ionic liquid works as the effective cathode electrode in the A-mode and the secondary electrons are emitted from the ionic liquid more efficiently than the SUS and Ni electrodes because the discharge voltage depends on the amount of the secondary electrons from the cathode electrode in the case of the usual dc grow discharge. In the B-mode, on the other hand, since the material of the cathode electrode is the same as in all cases of changing the anode materials, the discharge voltage-current characteristics do not change in spite of the various kinds of anode electrodes.

The increase in the discharge current in the case of the ionic liquid cathode in the A-mode is considered to be attributed to the concentration of the cathode sheath electric field on the ionic liquid surface which is reported to have a string shaped alkyl chain aligned toward the gas-phase region.[23] The concentration of the electric field causes the efficient ion irradiation to the ionic liquid, resulting in the emission of a large amount of secondary electrons from the ionic liquid surface more than the conventional metal cathodes such as SUS and Ni.

To investigate whether the species in the plasma is changed by the ion irradiation to the ionic liquid, optical emission spectroscopy (OES) spectra in the gas plasma region are measured as shown in Fig. 7 in (a) the A-mode and (b) the B-mode, where the ionic liquid is introduced in the glass cell. The spectrum peak at 390 nm, which corresponds to methylidyne radical (CH), is observed only in the A-mode [Fig. 7(a)]. The temporal evolutions of the spectrum peak intensities of CH normalized by those of Ar (751 nm) I_{CH}/I_{Ar} are presented in Fig. 8, and it is found that the CH peak intensity gradually increases with time only in the A-mode.

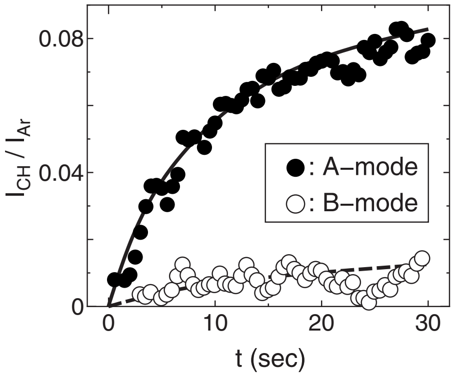

FIG. 8. Temporal evolutions of the spectrum peak intensities of CH (390 nm) normalized by those of Ar (751 nm) I_{CH}/I_{Ar}. $P_{gas}=20$ Pa, $I_D=1.5$ mA.

These phenomena can be explained by a process that the ion irradiation with high energy causes the dissociation of the alkyl-chain of the ionic liquid and the dissociated CH is transported to the gas plasma region from the ionic liquid region. In these OES spectra, we can find OH (308 nm) and H_α (656 nm) peaks in both the cases of the A- and B-modes. These peaks come from the tiny amount of water included in the ionic liquid as an impurity, which is evaporated and dissociated in the gas plasma region not only in the A-mode but also in the B-mode. This phenomenon is one of the evidence that the CH peak observed only in the A-mode is caused by the ion irradiation.

Figure 9 gives temporal evolutions of the temperature of the ionic liquid T_{IL} in the glass cell during the discharge in (a) the A-mode and (b) the B-mode. The ionic liquid temperature is about 20 °C before discharge. The stationary temperature of the ionic liquid is realized in the B-mode, while a slight increase in the temperature (~1 °C) is observed in the A-mode within 30 s, in which the CH peak is detected in the gas plasma region. However, the increment in the temperature is not large enough to evaporate the ionic liquid, because the temperature of at least 200–300 °C is necessary to evaporate the ionic liquid even under vacuum.[24] This little vaporization is confirmed by the temporal evolu-

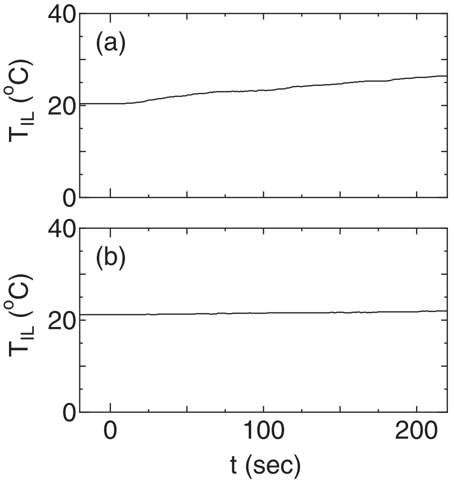

FIG. 9. Temporal evolutions of the temperature of the ionic liquid T_{IL} in (a) the A-mode and (b) the B-mode. $P_{gas}=80$ Pa, $I_D=1$ mA.

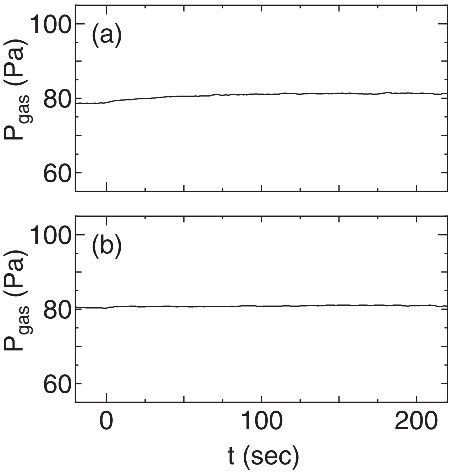

FIG. 10. Temporal evolutions of the gas pressure in the chamber P_{gas} in (a) the A-mode and (b) the B-mode. $I_D=1$ mA.

tion of the gas pressure P_{gas} in the chamber during the discharge as shown in Fig. 10. The gas pressure is originally adjusted to be 80 Pa and is found to be almost constant even during the plasma generation in both the cases of the A- and B-modes.

Based on these results, it is concluded that the reduction in the discharge voltage or the increase in the discharge current in the presence of the ionic liquid as the cathode electrode, and the observation of the CH peak in the gas plasma region only in the A-mode is caused by the ion irradiation to the ionic liquid. We emphasize that this controlled ion irradiation to the ionic liquid has the possibility to realize the effective physical and chemical reactions for the material synthesis at the static gas-liquid interface.

IV. CONCLUSION

A dc discharge plasma is generated just above the ionic liquid by applying the dc voltage to an electrode immersed in the ionic liquid against a grounded electrode set in the gas plasma region. The precise potential structure between these electrodes through the gas-liquid interfacial region is clarified for the first time, and the dynamics of the plasma ions is found to be controlled using the sheath electric field in the interfacial region. The ion irradiation to the ionic liquid and the resultant enhancement of the discharge due to the increase in the secondary electron emission from the ionic liquid are first demonstrated using our newly developed gas-liquid interfacial dc discharge plasmas.

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[1] J. Gubkin, Ann. Phys. **32**, 114 (1887).

[2] A. R. Denaro and A. Hickling, J. Electrochem. Soc. **105**, 265 (1958).

[3] Y. Kanzaki, M. Hirabe, and O. Matsumoto, J. Electrochem. Soc. **133**, 2267 (1986).

[4] T. Cserfalvi and P. Mezei, J. Anal. At. Spectrom. **9**, 345 (1994).

[5] M. Sato, T. Ohgiyama, and J. S. Clements, IEEE Trans. Ind. Appl. **32**, 106 (1996).

[6] B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, and J.-S. Chang, Ind. Eng. Chem. Res. **45**, 882 (2006).

[7] N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, and G. A. J. Amaratunga, Nature (London) **414**, 506 (2001).

[8] I. V. Lisitsyn, H. Nomiyama, S. Katsuki, and H. Akiyama, Rev. Sci. Instrum. **70**, 3457 (1999).

[9] K. Imasaka, J. Suehiro, Y. Kanatake, Y. Kato, and M. Hara, Nanotechnology **17**, 3421 (2006).

[10] J. Hieda, N. Saito, and O. Takai, J. Vac. Sci. Technol. A **26**, 854 (2008).

[11] S. Nomura and H. Toyota, Appl. Phys. Lett. **83**, 4503 (2003).

[12] T. Ishijima, H. Hotta, H. Sugai, and M. Sato, Appl. Phys. Lett. **91**, 121501 (2007).

[13] V. A. Ryzhkov, Physica B **323**, 324 (2002).

[14] T. Tomai, K. Katahira, H. Kubo, Y. Shimizu, T. Sasaki, N. Koshizaki, and K. Terashima, J. Supercrit. Fluids **41**, 404 (2007).

[15] K. Baba, T. Kaneko, and R. Hatakeyama, Jpn. J. Appl. Phys., Part 1 **45**, 8286 (2006).

[16] K. Baba, T. Okada, T. Kaneko, R. Hatakeyama, and H. Yoshiki, Thin Solid Films **515**, 4308 (2007).

[17] K. Baba, T. Kaneko, and R. Hatakeyama, Appl. Phys. Lett. **90**, 201501 (2007).

[18] S. A. Meiss, M. Rohnke, L. Kienle, S. Zein El Abedin, F. Endres, and J. Janek, ChemPhysChem **8**, 50 (2007).

[19] T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, and S. Kuwabata, Appl. Phys. Lett. **89**, 243117 (2006).

[20] F. Endres, D. MacFarlane, and A. Abbott, *Electrodeposition from Ionic Liquids* (Wiley-VCH, Weinheim, 2008).

[21] K. R. Seddon, Nature Mater. **2**, 363 (2003).

[22] R. D. Rogers and K. R. Seddon, Science **302**, 792 (2003).

[23] E. Sloutskin, B. M. Ocko, L. Tamam, I. Kuzmenko, T. Gog, and M. Deutsch, J. Am. Chem. Soc. **127**, 7796 (2005).

[24] M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, and J. A. Widegren, Nature (London) **439**, 831 (2006).